Cadmium Investigations in Lahore Soil and Other Regions of Pakistan

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Abstract. Cadmium (Cd) is toxic even in the very trace amounts and shows adverse effects on the human being and his environment. Current studies were performed to evaluate the Cd concentration in soil of Lahore (Pakistan) and the results were compared with those reported from other cities of Pakistan. The metal concentration evaluated by graphite furnace atomic absorption spectrometer (GFAAS). Cd concentration was found to be 1.39-20.82 µg/L, 1.38-93.60 µg/L, 2.42-94.60 µg/L, 2.25-93.98 µg/L and 1.15-8.14 µg/L in GT road, Misri shah, river Ravi, fertilized land of Raiwind side and unfertilized land of Raiwind side, respectively. The higher Cd concentration (2.42-94.60 µg/L) at "River Ravi" as compared to the other investigated areas (1.15-93.98 µg/L) is owed to the dumping of untreated waste from all industrial, sewage, domestic and agricultural zones in "River Ravi". The fertilized land was found to possess higher amount of Cd as compared to the unfertilized land. The awareness in farmers and the periodic monitoring of soil are important to eradicate the sources of Cd poisoning.

Keywords: cadmium (Cd), Lahore, river, fertilized/unfertilized land

Introduction

The toxicity of heavy metals is associated with severe health risks. They disturb the proper functioning of human body and are highly harmful for the environment (Jaishankar *et al*., 2014). Heavy metals including arsenic, cadmium, lead, chromium, nickel and mercury are important environmental pollutants, particularly in areas having industries or high anthropogenic pressure (Chaudhari *et al*., 2019; Iqbal *et al*., 2019; Rehman *et al*., 2019; Ullah *et al*., 2019; Olaniran *et al*., 2013). They cause serious problems to organisms and also bio-accumulation in the food chain (Waseem *et al*., 2014). Cd is a toxic heavy metal that may be detected in plants and soils (AbediMojiri, 2020). It is a widespread environmental pollutant which shows adverse effects on the human bones and kidneys, developmental effects in children, hormone related cancer in adults and cardiovascular diseases (Berglund *et al*., 2015). Cd is commonly present together with Pb, Cu and Zn ores and its concentration is easily increased in the environment due to volcanic activity and mining (Tabelin *et al*., 2018). Natural and anthropogenic sources e.g., municipal waste landfills, sewage sludge, phosphate fertilizers and mine/smelter wastes *etc* contribute to the Cd levels in soil and sediments. Cd and its compounds cause cancer of kidneys, lungs and prostate in humans (IARC, 2012) and severely affect renal, skeletal, urinary, reproductive and pulmonary systems (Rahimzadeh *et al*., 2017). Plants take up Cd from soil which ultimately reaches the human body through food chain. Human beings are directly exposed to Cd by inhalation and ingestion. After entering the human being, Cd may be accumulated in its body for the whole life and causes chronic and acute intoxications (Mahurpawar, 2015). It also demonstrates adverse effects on the enzymatic and oxidative processes and may cause nutritional deficiency in plants (Irfan *et al*., 2013). In the current studies, the Cd concentration has been investigated in the soil samples chosen from four major areas of Lahore (GT road, Misri shah, Ravi and Raiwind road) and results were compared with those reported earlier for other regions of Pakistan. Lahore was selected for Cd analysis and its control due to its heavy traffic, light and heavy industries, industrial and domestic sewage load.

Materials and Methods

The USS #10 sieves and locally prepared bottles of polyethylene and Teflon were used. The pyrex brand

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pipettes (5 mL), beakers (100 and 500 mL) and aluminum digestion blocks were used. Analytical grade chemicals (HNO_3, HCl, KI and Double distilled water) were employed. Throughout, the analytical work, double distilled water (DDW) was used. Graphite furnace atomic absorption spectrometer (GFAAS) of Model Varian 240 zeeman 120 auto sampler was used for metal analysis.

Sample collection. 100 samples of soil were collected from four most polluted areas of Lahore. Samples 1-20 were collected from Grand Trunk (GT) Road (location shown in Fig. S7A of Supplementary material) at a distance of 5-90 m, 21-41 from Misri Shah (Fig. S8A of Supplementary material), 42-61 from river Ravi (Fig. S9A of supplementary material), 62-80 from fertilized dairy farm near Raiwind and 81 to 100 from unfertilized farm near Raiwind, about 40 Km to the southeast of Lahore (Fig. S9C of supplementary material). The samples were thoroughly mixed in clean bags and then filtered with 2.5 mm pores, then the sample were put at 40 °C in an oven for a day.

Sample preparation, digestion and analysis. 2 g of each soil sample was bench dried for 5 days in the laboratory and then crushed in a mortar by a pestle. The fine ground sample was sieved through a 10-mesh (2 mm) sieve and moisture was dried in the oven separately at 105 °C until constant weight was achieved. The wet digestion was done by reflux digestion of 1 g sub-sample with 10 mL of concentrated HCl/HNO_3 in 1:4 ratios. A few boiling chips were added and the temperature was regulated at 100 °C for 3 h by using Aluminum digestion block. The mixture was cooled and washed with 12.5% V/V HNO_3 followed by filtration. Cd analysis was performed by Graphite furnace Atomic absorption Spectrometry (GFAAS). With each sample set, a reference material and two blanks were also run. All analyses were performed in triplicates and their mean values were calculated. For elimination of matrix interferences, 10% V/V potassium iodide solution was added to all standards and sample solutions.

Results and Discussion

The soil samples were analyzed for Cd by using GF AAS; the obtained data are summarized in Tables 1-5 and Fig. 1-6. The concentration of Cd along GT road (samples 1-20) was found in the range of 1.39-20.82 µg/L (Table 1), it was lying within the safe limits (32000 µg/L) of WHO. The concentration of Cd in the soil surface was found higher as compared to the soil taken from lower depths, due to the direct exposure of Cd on the soil surface. As shown in Fig. 1, sample no 3 (collected from Zaitoon Colony) shows maximum conc. of Cd near Sue Wala road because this area has many factories including Speed Packages (Fig. S7B in supplementary material), Sartaj shoes *etc*. Sample 9 has minimum Cd concentration as it was taken from Sharif Garden area which is a non-factory zone. So, it can

Table 1. Cd concentration along GT road (from Zaitoon colony to Sharif garden (5-90 m)

Sample no.	Conc. of Cd	SD calculated	Sample no.	Conc. of Cd	SD calculated
1	1.80	±0.01	11	2.44	±0.01
2	10.46	±0.19	12	1.89	±0.02
3	20.82	±0.65	13	1.70	±0.10
4	2.99	±0.11	14	1.63	±0.01
5	9.67	±0.48	15	3.61	±0.08
6	1.86	±0.02	16	6.51	±0.02
7	2.35	±0.14	17	4.37	±0.08
8	2.30	±0.07	18	5.38	±0.23
9	1.39	±0.02	19	4.09	±0.06
10	1.95	±0.02	20	4.93	0.10

Statistical analysis (one way ANOVA) has shown significant results (P<0.05)

Source of variation	SS	df	MS	F	P-value	F crit
Between groups	347.2745	1	347.2745	12.34869	0.001158	4.098172
Within groups	1068.65	38	28.12236			
Total	1415.924	39				

easily be concluded that soils of factory areas have higher Cd concentration (sample no 2 and 3) as compared to the non-factory areas.

The amount of Cd (Table 2 and Fig. 2) in Misri Shah areas (samples 21-41) ranges from 1.38-93.60 µg/L and lies within the safe limits (32000 µg) of WHO. The existence of Ni-Cd battery manufacturing units are direct sources of Cd in the soil of this area. However, the Cd level was varied among all the tested samples of this region. Sample no 34 (Fig. 2) was rich in Cd as it was collected from Kucha Rahim road having a lot of factories like Inam Steel Re Rolling Mill (Fig. S8B, supplementary material), water treatment plant and battery manufacturingindustries etc. The samples 36 and 37 had shown minimum Cd concentration as these were collected from Akbar road areas which had only Mubarak battery agency but surrounded by a lot of bakeries. As compared to GT road, soil of Misri Shah is more contaminated with Cd due to the presence of battery agencies, numerous cottage industries and heavy traffic.

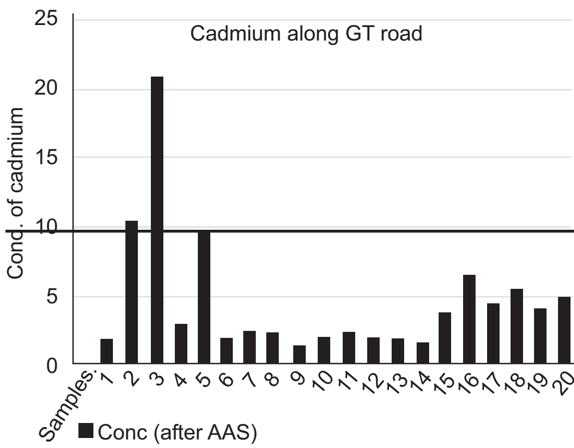

Fig. 1. Cd concentration along GT road.

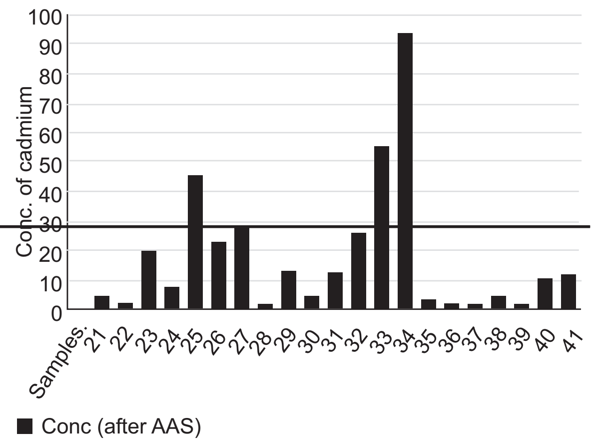

Fig. 2. Cd concentrations in Misri Shah.

Table 2. Cd concentration in Misri Shah areas (Kacha Rahim Road to Akbar Road (10-160 m)

Sample no.	Conc. of Cd	SD calculated	Sample no.	Conc. of Cd	SD calculated
21	4.68	±0.24	32	25.40	±2.40
22	2.21	±0.08	33	55.20	±3.60
23	19.51	±1.00	34	93.60	±16.30
24	7.64	±2.30	35	3.31	±0.11
25	45.15	±0.05	36	1.38	±0.01
26	22.40	±0.80	37.	1.48	±0.03
27	28.00	±0.10	38	4.15	±0.07
28	1.91	±0.02	39	2.10	±0.03
29	12.97	±1.76	40	10.60	±0.20
30	4.67	±0.03	41	11.85	±0.45
31	11.80	±0.40			

Statistical analysis (one way ANOVA) has shown significant results (P<0.05)

Source of variation	SS	df	MS	F	P-value	F crit
SS	df	MS	F	P-value	F crit	
Between groups	1879.89	1	1879.89	6.762	0.01	4.08
Within groups	11116.22	40	277.90			
Total	12996.11	41				

The amount of Cd in river Ravi soil (samples 42-61) was ranged from 2.42-94.60 μg/L (Table 3 and Fig. 3) which lies in the safe limit (32000 μg) recommended by WHO. Ravi soil was found more contaminated with Cd as compared to GT road and Misri Shah. The samples 55, 50 and 59 have shown maximum Cd conc. (Fig. 3) because they belonged to the areas, where waste water from different factories, industries, sewage and agricultural sites is damped into river Ravi. Approximately 14 main drain, 100 industrial units along with 31-36 textile industries and tannery units discharge their wastes into Ravi on daily basis thus making it rich in Cd. Moreover, PSO filling station is the main source of Cd. Figure S9B (supplementary material) shows the dumping of waste material from Hudiara Drain (a great source of pollution for Ravi river). While sample no 49 and 57 were collected near the areas of river Ravi which were near green belt.

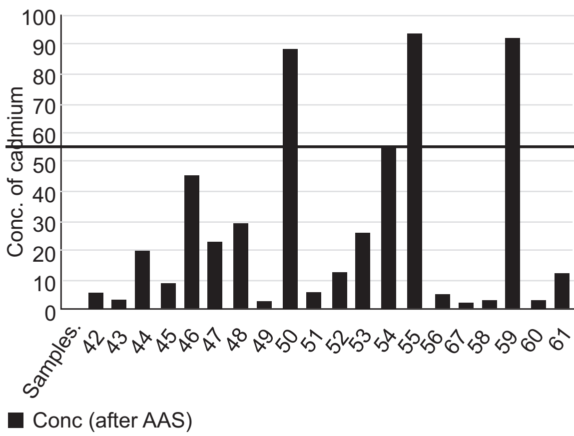

Fig. 3. Cd concentration in river Ravi.

The Cd concentration for the samples 62-80 (fertilized dairy farm near Raiwind) and samples 81-100 (unfertilized farm near Raiwind) have been displayed in Table 4 and Fig. 4-5.

Figure 4 indicates that the amount of Cd in fertilized farms ranges from 2.25-93.98 μg/L and lies in the safe level (32000 μg) as recommended by WHO. The highest conc. of Cd was observed for sample 75. The presence of Cd in the soil of fertilized farms was owed to the use of phosphate fertilizer which enhances the uptake of Cd by plant and consequently its entry in the food chain. Actaully phosphate compounds help in the assimilation and storage of Cd in the plants. Figure 5 indicates that the amount of Cd in unfertilized land ranges from 1.15-8.14 μg/L which is very low (2.25-93.98 μg/L) as compared to the fertilized land of the same area. Unfertilized soil has less amount of Cd due the absence of phosphate fertilizer and other source of Cd.

Table 5 and Fig. 6 demonstrate the comparison between Cd concentrations measured in various areas of Lahore. The mean Cd concentration in the area of river Ravi is much greater (94.6 μg/L) than any other place in Lahore; the reason is that Cd salts tend to sediment more in anoxic environment.

Table 3. Cd concentration in river Ravi (10-200 m)

Sample no.	Conc. of Cd	SD calculated	Sample no.	Conc. of Cd	SD calculated
42	5.68	±0.32	52	12.80	±0.50
43	3.21	±0.10	53	26.00	±2.43
44	20.10	±1.03	54	56.20	±3.78
45	8.64	±2.36	55	94.60	±16.40
46	46.13	±0.06	56	4.51	±0.21
47	23.40	±0.81	57	2.42	±0.02
48	29.25	±0.12	58	2.85	±0.03
49	3.02	±0.03	59	93.15	±15.00
50	90.25	±1.86	60	3.10	±0.04
51	5.77	±0.05	61	11.70	±0.22

Statistical analysis (one way ANOVA) has shown significant results ($P<0.05$)

Source of variation	SS	df	MS	F	P-value	F crit
Between groups	5934.583	1	5934.58	11.28	0.001	4.09
Within groups	19979.48	38	525.77			
Total	25914.06	39				

Table 4. Cd concentration in the soil of fertilized and unfertilized farms near Raiwind

Sample no.	Conc. of Cd	SD calculated	Sample no.	Conc. of Cd	SD calculated
Fertilized farm			Unfertilized farms (10-200 m)		
62	5.00	±0.30	81	1.20	±0.01
63	76.66	±9.10	82	7.46	±0.17
64	20.00	±1.00	83	8.14	±0.60
65	8.12	±2.30	84	1.99	±0.10
66	45.50	±0.05	85	8.50	±0.42
67	22.50	±0.80	86	1.88	±0.01
68	28.90	±0.11	87	1.23	±0.12
69	2.75	±0.02	88	1.22	±0.06
70	71.47	±1.83	89	1.15	±0.01
71	5.15	±0.04	90	1.90	±0.01
72	11.9	±0.45	91	2.32	±0.01
73	25.96	±2.00	92	1.99	±0.02
74	55.90	±3.11	93	1.63	±0.12
75	93.98	±16.00	94	1.60	±0.02
76	4.00	±0.20	95	3.00	±0.07
77	72.65	±0.01	96	2.05	±0.03
78	2.25	±0.02	97	2.28	±0.06
79	4.98	±2.00	98	3.05	±0.21
80	2.89	±0.04	99	2.89	±0.04
			100	1.99	±0.11

Statistical analysis (one way ANOVA) has shown significant results (P<0.05)

Source of variation	SS	df	MS	F	P-value	F crit
Between groups	76212.84	1	76212.84	209.84	0	3.98
Within groups	24696.97	68	363.19			
Total	100909.8	69				

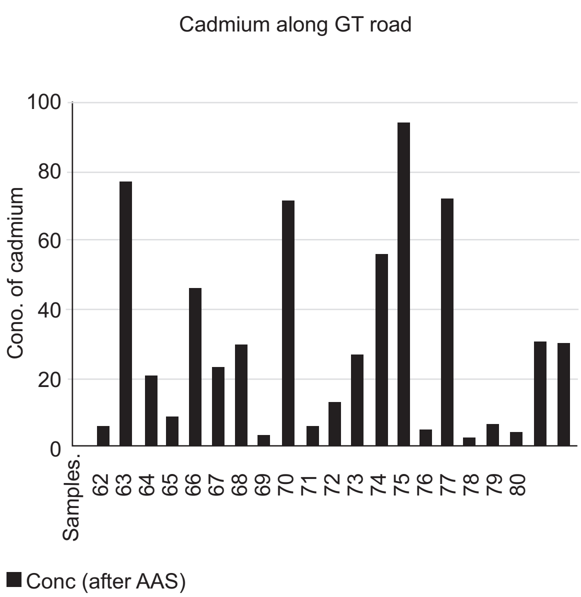

Fig. 4. Cd concentration in fertilized farm.

Table 5. Comparison of concentration of Cd in different areas of Lahore

Locations mean conc. of Cd	SD calculated	
GT road	20.82	±0.65
Misri Shah	93.60	±16.30
River Ravi	94.60	±16.40
Fertilized farms	93.99	±16.00
Unfertilized farms	8.50	±0.42

Statistical analysis (one way ANOVA) has shown significant results (P<0.05)

Source of variation	SS	df	MS	F	P-value	F crit
Between groups	8791.818	1	8791.81	9.19	0.01	5.31
Within groups	7652.266	8	956.53			
Total	16444.08	9				

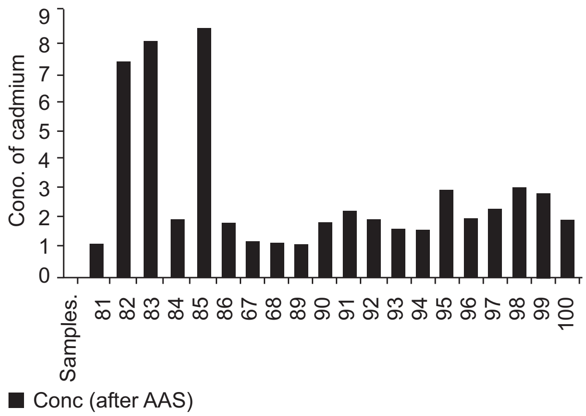

Fig. 5. Cd concentration in unfertilized farms.

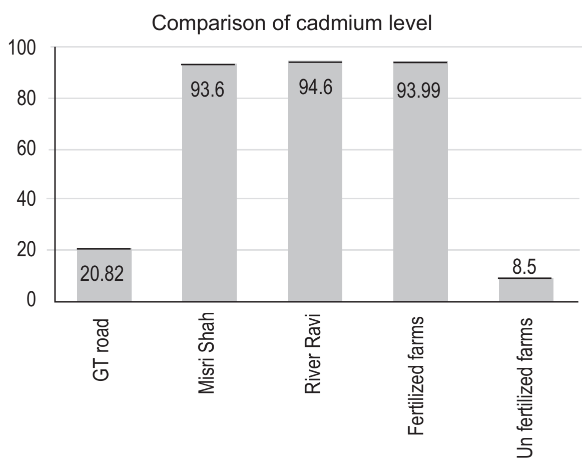

Fig. 6. Comparison of concentration of Cd in the five different localities of Lahore.

If we compare the above results with those obtained from other regions of the country (Pakistan) then it may easily be concluded that Cd concentration varies greatly from the region to region throughout the country. The literature also shows seasonal variations in Kalar Kahar lake, Chakwal (Pakistan), it is undetectable in the months of March-April, but reaches to 0.01-0.05) mg/L in other months (Raza *et al*., 2007). The maximum recommended concentration of Cd in drinking water is 0.005 mg/L as suggested by set by WHO (Kumar and Puri, 2012), this value ranges from 0.001 to 0.21 mg/L as reported from various sites of Pakistan (Lone *et al*., 2003). The drinking water contaminated with heavy metals such as Cd is becoming a major health concern today (Rehman *et al*., 2018) and such a kind of water poses health risks (Ayandiran *et al*., 2018). Cancer risks have been reported due to ingestion of such water (Fakhri *et al*., 2018). The exposure to Cd in the presence of Al shows more adverse health effects on humans and kidneys are mainly effected *via* food and non-food items (Panhwar *et al*., 2016). The highest concentration of Cd (0.21 mg/L) with an average of 0.02 mg/L was observed from the tube well water samples of Hayatabad Industrial Estate, Khyber Pakhtunkhwa (KPK) (Manzoor *et al*., 2006). The excess level of Cd in drinking water of Pakistan, may be rendered to the effluent discharges of mining, metal plating and the industries of marbles, steel and aluminium (Nazir *et al*., 2015). The Cd concentration ranges from 0.002 to 0.09 mg/L (mean 0.02 mg/L) in surface water samples of KPK province with the highest value observed in Kalpani drain. It lies in a range of 0.002 and 0.07 mg/L Cd (mean 0.04 mg/L) in Malir river of Karachi in Sindh province (Tariq *et al*., 2006). Cd distribution also various in wastewater of different regions in Pakistan. The wastewater in Gadoon Amazai Industrial Estate, Swabi (KPK province) demonstrated the Cd concentration in a range of 0.19-0.62 mg/L (Khan *et al*., 2009). The mean Cd concentration (0.03 mg/L) from seven sites of river Kabul near Peshawar (Pakistan) in 2009, was found under the standard limits (Ullah *et al*., 2013). The Korangi area, Karachi demonstrated the highest concentration (5.35 mg/L) of Cd (Saif *et al*., 2005), this concentration was exceeded the permissible limit of 0.10 mg/L set by NEQS-Pak for sewage and industrial wastewater (Waseem *et al*., 2014). Furthermore, in east and north zones of Lahore (Punjab province) the concentration of Cd (0.18 to 0.37 mg/L) in wastewater also exceeds the above the safe limit set (Mahmood and Malik, 2014). The highest Cd concentration (24.34 mg/Kg) in sediments was reported in Gizri creek location at the most downstream part of the Malir river, Karachi, the second highest value (21.34 mg/Kg) was observed in the Lyari location (Karachi), where the Lyari river drains the city waste into the Arabian sea (Siddique *et al*., 2009). The Cd concentration was found lower as compared to recommended limits in water sources from tap water, tube wells and storage tanks of Kohat city, Lachi and Shakardara of district Kohat, Khyber Pakhtunkhwa (Pakistan) (Iqbal *et al*., 2014). In the sediments of the, Punjab province, the mean Cd concentrations was fluctuated between 0.99 mg/Kg (Lahore Siphon) and 3.17 mg/Kg (Shahdera Bridge) in river Ravi sediments of Lahore (Punjab province) (Abdul *et al*., 2009). Toxic metals gain entry in the human body by inhalation of dust, consumption of contaminated water and food crops (Ali *et al*., 2019). The transfer of heavy metals from soil to food crops or vegetables has been commonly suggested in Pakistan (Mahmood and Malik, 2014; Hassan *et al*., 2013). Cd is accumulated more in dicots as compared to monocots (Murtaza *et al*., 2015). Studies on soils and vegetables of different areas in Pakistan suggested that the lowest concentration (0.15 mg/Kg) of Cd was found in Hangu soil whereas the highest (3.43 mg/Kg) was in DI Khan soils. The vegetables of these regions contained the Cd concentration from 0.2 to 1.6 mg/Kg and different vegetables have different accumulation rates of Cd. The highest concentration was suggested due to extensive use of and pesticides, manures and phosphate fertilizers. Consumption of such vegetables results in a serious health risk for the local community (Rehman *et al*., 2017). The maximum recommended concentration of Cd is 0.05 mg Cd/Kg by weight in fresh vegetables (Ercilla-Montserrat *et al*., 2018). Cd has very high rate of penetration into the leaves, so when it is absorbed by the plant it is suddenly reached into the leaves (Pennisi *et al*., 2016). Thus Quetta city, Balochistan province, a critical toxic level (5.63 mg/Kg, average) of Cd in lettuce irrigated with wastewater effluents was reported (Achakzai *et al*., 2011). The mean concentrations of Cd in Gilgit (Northern Pakistan) ranges from 0.24 to 2.1 mg/Kg in all vegetable samples, being the lowest concentration in *M. sylvestris* and the highest in *S. oleracea* (Khan *et al*., 2010). Heavy metals in present in air are directly inhaled into the lungs through respiration. So, the Cd concentration in atmosphere is of great concern, the safe limit according to WHO is 5 ng/m^3 in air (Ercilla-Montserrat *et al*., 2018). This value lies in the safe limit in Pakistan except few regions *i.e*., in Lahore where, the annual mean Cd concentration has been reported to be 69 ng/m^3 in particulate matter ($PM_{2.5}$) (von Schneidemesser *et al*., 2010).

Possible remedies. Following measures should be taken by Government of Pakistan:

(1) Factories manufacturing Ni/Cd should be planted far away from residential areas like Misri Shah.
(2) The disposal of industrial and domestic waste into water bodies like river Ravi should be stopped.
(3) The use of phosphorous fertilizer in animal grazing farms should be minimized.
(4) Zn mining should be monitored properly because it is the major source of Cd in soil.
(5) The cultivation of vegetables like spinach in polluted water should be stopped.
(6) The government of Pakistan should took effective measures to implement points 1-4 and for installation of factories away from residential areas.

Proper strategies should be formulated by Government departments for regular monitoring of food crops and the soils in order to ensure the safety of food (Rehman *et al*., 2017). Biochar and rice husk have been reported to decrease the metal uptake by plants by adsorption phenomenon (Khan *et al*., 2018). The awareness programmes for the exposed people and public education is highly important in this regard to prevent from Cd poisoning (Rahimzadeh *et al*., 2017).

Supplementary material.

- **Fig. S7 A and B.** (A) Map showing location of sampling from Zaitoon colony to Sharif garden (GT road), (B) Speed packages (Lahore) produces Cd smoke in the atmosphere.
- **Fig. S8 A and B.** (A) Map showing location of sampling from Kacha Rahim road to Akbar road; (B) Inam Steel Re Rolling Mill furnace producing Cd as by product.

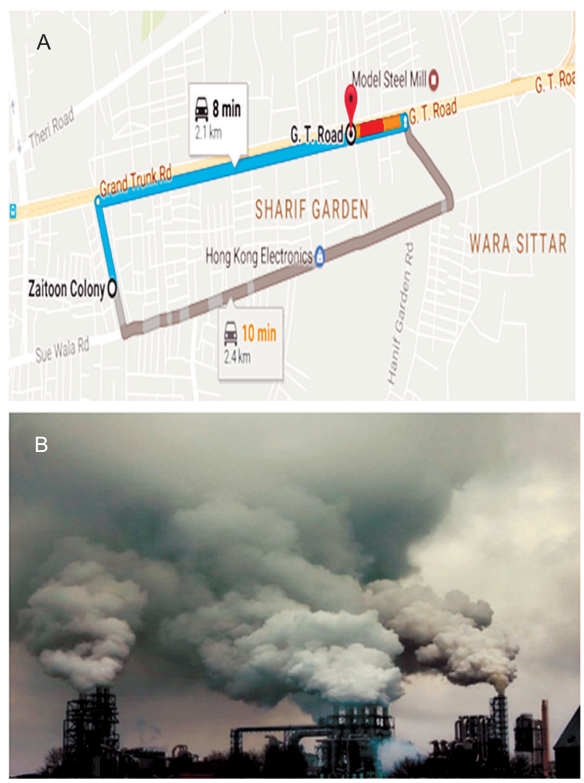

Fig. S7 A&B. (A) Map showing location of sampling from Zaitoon colony to Sharif garden (GT road); **(B)** speed packages (Lahore) produces Cd smoke in the atmosphere.

- **Fig. S9 A and C.** (A) Map showing location of sampling (river Ravi); (B) Dumping of wastes from Hudiara drain (Great pollution source for Ravi river); (C) Map showing Raiwind road.

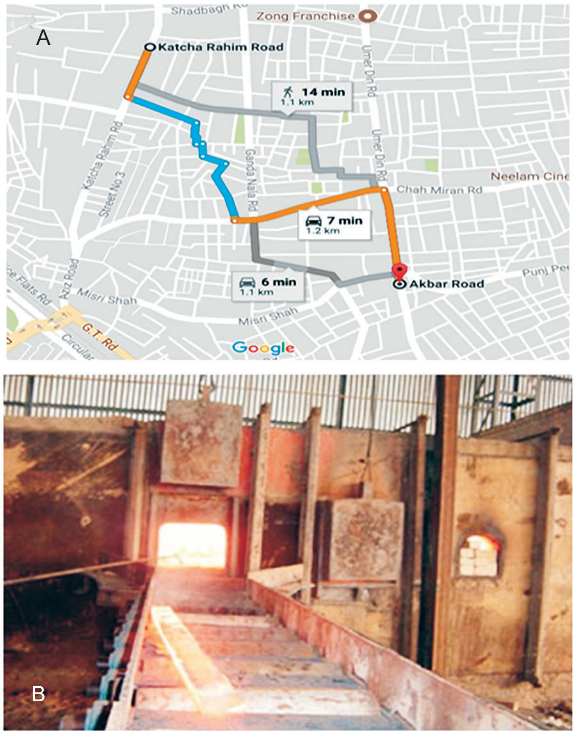

Fig. S8 A-B. (A) Map showing location of sampling from Kacha Rahim road to Akbar road; **(B)** Inam steel re rolling mill furnace producing Cd as by product.

Conclusions

Cd is one of the toxic heavy metals which need special attention in populated areas. Its concentration was measured in various regions of Lahore (Pakistan) and was found to be 1.39-20.82 µg/L, 1.38-93.60 µg/L, 2.42 -94.60 µg/L, 2.25-93.98 µg/L and 1.15-8.14 µg/L in GT road, Misri Shah, river Ravi, fertilized land of Raiwind side and unfertilized land of Raiwind side, respectively. The mean Cd concentration in the area of river Ravi was found much greater (94.6 µg/L) than any other place in Lahore because Cd salts tend to sediment more in anoxic environment. The fertilized land was found to possess higher amount of Cd as compared to the unfertilized land. The government of Pakistan should adopt proper strategies to prevent excessive accumulation of Cd in soil. The awareness

Fig. S9 A-C. (A) Map showing location of sampling (river Ravi); **(B)** Dumping of wastes from Hudiara drain (Great pollution source for Ravi river); **(C)** Map showing Raiwind road.

in farmers and the periodic monitoring of soil are important to eradicate the sources of Cd poisoning.

Conflict of Interest. The authors declare no conflict of interest.

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